

AD611558

DDC AVAILABILITY NOTICE

Qualified requestors may obtain copies of this report from DDC. This report be released to OTS.

FUEL CELL

RESEARCH & DEVELOPMENT

COPY	2	OF	3	12
HARD COPY				\$. 2.00
MICROFICHE				\$. 0.50

32P

SATURATED HYDROCARBON FUEL CELL PROGRAM

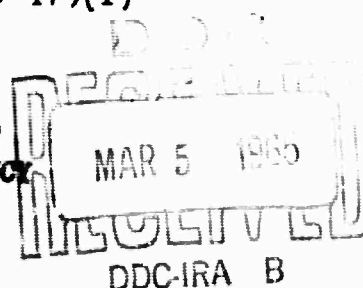
A NEW HIGH PERFORMANCE FUEL CELL EMPLOYING
CONDUCTING-POROUS-TEFLON ELECTRODES
(NIEDRACH-ALFORD) AND LIQUID ELECTROLYTES

CONTRACT NUMBER DA44-009-AMC-479(T)

ARPA ORDER NUMBER 247

PROJECT NUMBER P4980

THE VIEWS CONTAINED HEREIN REPRESENT
ONLY THE VIEWS OF THE PREPARING AGENCY
AND HAVE NOT BEEN APPROVED BY THE
DEPARTMENT OF THE ARMY.



U.S. ARMY
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
FT. BEL VOIR, VIRGINIA

DIRECT ENERGY CONVERSION OPERATION

GENERAL  ELECTRIC

LYNN, MASS.

ARCHIVE COPY

FORWARD

This report is delivered by the Direct Energy Conversion Operation, General Electric Company as a contractual item under its Direct Hydrocarbon Fuel Cell Program which is being conducted for the U.S. Army Engineer Research and Development Laboratories, Contract Number DA44-009-AMC-479(T). The report consists of two parts:

1. A detailed description of the concept, principles of operation and fabrication of the high performance Niedrach-Alford Fuel Cell Electrodes.
2. Appendix 1 - Patent Application Specification.

A New High Performance Fuel Cell Employing Conducting-Porous-Teflon Electrodes and Liquid Electrolytes

L. W. Niedrach and H. R. Alford
General Electric Research Laboratory
Schenectady, New York

ABSTRACT

A low temperature, aqueous electrolyte fuel cell employing new, Conducting-Porous-Teflon Electrodes is described. The new electrodes show excellent performance characteristics with a variety of fuels (including hydrocarbons) and with both oxygen and air as the oxidant. Preparation methods are discussed, and performance data obtained with ambient temperature, hydrogen-oxygen and hydrogen-air cells are presented to illustrate their properties.

INTRODUCTION

In earlier publications the use of "Conducting-Porous-Teflon Electrodes" in regenerative, matrix-type cells has been described (1, 2). While these cells are of some interest, particularly for applications in gravity-free space, they have not been given serious consideration for operation on a continuous feed basis. Under the latter conditions the matrix is responsible for some operational disadvantages; e. g., at high current densities concentration polarization can occur at the electrodes, maintenance of the proper water balance in the electrolyte introduces design problems, and the internal resistances of the cells are higher than desired. In order to overcome these difficulties, work was directed at modifying and improving the original electrode structure so that the matrix could be eliminated. This has resulted in a new, high-performance fuel cell which operates with an aqueous electrolyte.

In seeking this objective two important restrictions concerning operation were deliberately imposed as being desirable: 1) The fuel (oxidant) gas-electrolyte interface was to be established within the electrode structure by "controlled wetting", and, 2) the electrodes were to be capable of operation at ambient atmospheric pressure. In addition, emphasis was placed upon retaining a relatively thin structure.

The new electrodes which are 5 to 10 mils thick, consist of a Teflon-catalyst mix that is pressed and sintered onto a suitable supporting screen which also serves as an excellent electronic conductor to carry current to the terminals of the cell. A porous Teflon film on the gas side of the electrode provides for proper control of wetting so that both the electrolyte and reacting gas have satisfactory access to the highly developed surface of the electrode. While alternative means of preparing electrodes were considered - e.g., use of high Teflon-to-catalyst ratios and laminar structures with two different Teflon-to-catalyst ratios - the results obtained with the film covered electrodes were by far the most encouraging. These electrodes were found to be exceedingly reliable and readily manufactured in the laboratory. It was therefore elected to concentrate on electrodes of this type, and they serve as the basis of the present paper which is devoted to a discussion of their preparation and properties as exemplified by their performance in ambient temperature, hydrogen-oxygen and hydrogen-air cells. Platinum black was used almost exclusively as the electrocatalyst in the work to be reviewed and 6 N KOH and 5 N H_2SO_4 were the principal electrolytes.

The electrodes are exceedingly versatile and some performance data obtained with other fuels and electrolytes have already been published. Thus, excellent performances have been reported for a variety of hydrocarbons, with a sulfuric acid electrolyte up to 89°C. (3, and with a phosphoric acid electrolyte up to 200°C. (3, 4, 5). In addition, they have also been used effectively with methanol and a cesium carbonate electrolyte at temperatures up to 185°C (6).

STRUCTURE OF THE NEW ELECTRODES

Examples of the new electrodes are shown in Fig. 1. These were prepared by bonding platinum black-Teflon mixtures to the central areas of nickel screens. One quarter-inch-wide rings of 5-mil-thick Teflon sheet (duPont's FEP Fluorocarbon Film) were used as seals around the peripheries. In mounting the electrodes in cell housings these seals are buried under the gaskets that are used. In another version the outer ring has been eliminated and the catalyst-Teflon mix has been spread uniformly over the entire circular area of the screen. Such electrodes perform equally well electrically, and retain the electrolyte more reliably.

The important differences in the two surfaces of the electrodes are shown clearly in Fig. 1. The surface of the electrode on the left is coated with the porous Teflon film and is obviously exceedingly hydrophobic. In operation this side faces one of the gases. The untreated, electrolyte side of the electrode on the right has been wetted by drops of water placed upon it.

The photomicrographs in Figs. 2 and 3 bring out additional details of the electrode structure. That in Fig. 2 is a reflection micrograph of a section through an electrode. It shows the surface film clearly at the top. As shown by the wire at the left, the screen is entirely imbedded in the catalyst-Teflon mix. Fig. 3 is a transmission electron micrograph obtained from a microtomed cross section. Again the surface film can be seen clearly, and a better indication of the catalyst distribution is obtained. It is pertinent to note here that the starting catalyst consists of agglomerates of particles about 0.01 microns in size. The ultimate size of the Teflon particles is about 0.2 to 0.5 microns.

EXPERIMENTAL

Preparation of Electrodes

Most of the electrodes used in this work were prepared by a standard procedure. A Teflon suspension (duPont's Teflon-30, which contained 59.6 percent solids by weight) was the source of the binding material. Platinum black from Engelhard Industries, Inc., was used as the catalyst in most cases, but a few other catalysts were also used. Several different screen materials were employed, but those listed in Table I were found most useful.

TABLE I

Reinforcing Screens Used In Electrode Fabrication

<u>Metal</u>	<u>Mesh</u> <u>(wires/inch)</u>	<u>Wire Size</u> <u>(diameter, mils)</u>
Platinum	80	3
	45	7.8
Nickel	40	4.5
Silver	40	7.5

While electrodes can be made with finer mesh screens of smaller wire size, it has been found that their resistances are high enough to be unattractive. In most of the work, therefore, 40- to 45-mesh screen made of 5- to 8-mil wire was used. In order to minimize the thickness of the electrodes, such screens were regularly rolled to a thickness corresponding to that of the individual wires. It was found necessary to leave wide tabs on the screens in order to reduce ohmic losses during operation of cells at high current densities.

Before making the electrodes themselves, a supply of Teflon films was prepared for use as surface coatings. This was done by spraying a Teflon-30 suspension diluted with seven volumes of water onto an aluminum foil using an air brush (Paasche, Type V). Films corresponding to 0.79, 1.6, 2.4, and 3.9 mg Teflon per cm^2 were used. In preparing these films a 5- by 5-inch square area was marked on the aluminum foil and an appropriate amount of the diluted Teflon suspension was used to coat this area to the desired thickness. Before spraying, a pattern of four circles having the diameter of the ultimately desired electrodes was scribed within the square to facilitate later steps in the preparation.

A fine spray was used so that several retracings of the pattern could be made in order to obtain a uniform thickness. During application, the aluminum foil was mounted on the bed of a hot plate which was maintained at 120° to 150°C to facilitate evaporation of the water from the spray. The rate of application was such that wet areas did not develop and run on the foil.

Following the spraying, the foil was placed on the bed of the press (6-inch bed Carver press with individually heated platens) at 350°C and the jaws were closed to a gap of about $1/8$ inch for about a minute. During this treatment the non-ionic wetting agent in the Teflon suspension was rejected, and sintering of the Teflon particles occurred to form the desired film (6a).

Spreads of platinum black (or other catalyst) with the Teflon-30 suspension were then prepared on circular areas on two aluminum foils - one of which had previously been coated with Teflon as described above. In preparing a typical spread to cover the entire circular area of the screen (17.7 cm^2), a 0.03-cc aliquot of the Teflon-30 suspension was first placed on the foil along with a suitable volume of dilution water, about 0.6 cc. After mixing, 0.3 gram of platinum black (previously sifted through a 325-mesh screen) was added and a thin, cream-like slurry was made by mixing with a small spatula. This was then dispersed as uniformly as possible over the area and slowly dried on a hot plate. It was necessary to raise the temperature very slowly during the initial phases to obtain a satisfactory deposit. Ultimately, however, the bed of the hot plate was raised to 250 to 350°C to dispel the wetting agent as white fumes from the Teflon suspension.

The screen having a tab was then centered over one of the spreads, a strip of Teflon sheet was placed across the tab as a seal, and then the second spread was centered over the first. This assembly which was sandwiched between two ferrotype plates was then placed on the bed of the press. Sintering was performed at 350°C for 2 minutes at the desired pressure - usually 1800 to 3000 lb. per in^2 of electrode surface.

Following the heat treatment, the aluminum foil was dissolved from the electrode with warm 20% NaOH. A water rinse and an air drying then resulted in a finished electrode. In most of the work, electrodes - either with or without the peripheral Teflon rings - were prepared as outlined above. The occasional variations that were introduced will be described as they arise.

Test Cell

The completed electrodes were housed as shown in the exploded view of a cell in Fig. 4. The two electrodes were separated by a 1/8-inch-thick spacer which formed a 1 1/2-inch-diameter pocket for the free electrolyte. Appropriate gaskets and face plates formed chambers for the fuel and oxidant gases. All plastic parts were of Lucite, and gaskets were of silicone rubber or poly(ethylene-butene) copolymer. Gasketing was such that the effective working areas of the electrodes were 1 1/2-inch-diameter circles. Platinum and Teflon tubing were used for the connections that encountered electrolyte. Gases were flowed through polyethylene tubing. For operation on air one of the faceplates contained a 1 1/2-inch-diameter hole. This gave free access of air to the electrode.

Electrolytic hydrogen and purified oxygen were employed during operation. At low current densities static gases could be used, but at high current densities ($> 250 \text{ ma/cm}^2$) it was generally found desirable to maintain slow flows of the gases through a cell. This was particularly true of the oxygen which contained enough nitrogen and argon as impurities to accumulate rapidly in the cell chambers and cause "smothering."

In order to prevent the water produced in the cell reaction from diluting the electrolyte excessively, the electrolyte was circulated between the cell and a relatively large reservoir. In initial experiments, forced circulation was achieved by means of gravity flow from a reservoir above the cell level. Electrolyte which drained from the cell was then returned to the reservoir with the aid of a Teflon bellows pump.

It was soon found that the circulation provided by means of a thermal loop was adequate to maintain the cell performance. This simpler arrangement was therefore used for most of the work. A polyethylene bottle connected to the cell with Teflon tubing serving as the reservoir.

A reference electrode was prepared by mounting one of the new type electrodes in a separate housing and exposing one side to hydrogen. Electrolyte in the other chamber of the reference cell then made contact with the working system, via a bridge of Teflon tubing filled with the common electro-

lyte. Individual electrode performances in the cell under test were then obtained vs. the reference from measurements with a Kordes-Marko bridge (7). Use of the bridge also permitted the measurement of IR-free voltages.

Although most of the measurements were made with the aid of the Kordes-Marko bridge, overall polarization curves were frequently obtained during direct discharge of cells through resistive loads. These invariably agreed well with the overall curves obtained with the pulsating current derived from the bridge.

RESULTS AND DISCUSSION

General

Before examining the effects of a number of individual parameters, it is of interest to consider the general performance characteristics of the new cells with alkaline and acidic electrolytes. For this purpose polarization curves are shown in Figs. 5 and 6. It is significant to note that current densities as high as 1000 ma/cm^2 have been delivered by alkaline cells operating on hydrogen and oxygen. While the voltage (and hence efficiency) is low at these high current densities, the linearity of the polarization curve gives assurance that the new electrodes will be able to handle surge currents well above the 100 to 200 ma/cm^2 that might be considered as the normal operating range. The performance of hydrogen-oxygen cells with acidic electrolytes is similar to, but generally somewhat inferior to, that observed with the alkaline electrolyte.

Even when air is used as the oxidant, relatively high current densities can be obtained with the new cell before evidence of mass transfer polarization appears in the form of a sharp decline in the voltage with increasing load. The somewhat lower cell voltages observed when air is substituted for oxygen appears to be, at least partially, related to the fact that better cooling is accomplished during air operation. As a result, internal resistances are higher and electrode reactions are more sluggish than when oxygen is used and higher temperatures are reached in the cell. In this connection it can be noted that electrolyte and electrode temperatures of about 70°C have been measured on both acidic and alkaline, hydrogen-oxygen cells at current densities of about 500 ma/cm^2 . Under these conditions 10-degree rises in the temperatures of the electrolytes in the reservoirs were observed. This attests to a reasonable degree of electrolyte circulation between the cells and their reservoirs.

In spite of their thinness, the new electrodes can also do an excellent job of retaining the aqueous electrolytes. A small amount of seepage has, however, been observed with all the electrodes tested to date. In practice then, it may be necessary to provide some means of recycling the seepage.

Effect of the Thickness of the Surface Film

The first series of experiments was devoted to an examination of the effect of the thickness of the Teflon surface film on cell performance. All electrodes used in this series were prepared with rolled 40-mesh nickel screens having wire diameters of 4.5 mils. Two identical electrodes with peripheral Teflon rings were used in each of the test cells. Surface films of 0.79, 1.6, 2.4, and 3.9 mg Teflon/cm² were tested. All of the experiments were performed with alkaline electrolytes, 6 M KOH. Most of the polarization data shown in Figs. 7 and 8 were obtained with the Kordes-Marko bridge and show the potentials of the fuel and oxidant electrodes against the hydrogen reference. Also shown are the overall performance curves (iR drop included) for the cells operating on oxygen and on air. At the time that these tests were made, the bridge could handle a maximum current of about 4.5 amperes. The data obtained at higher current densities were therefore obtained by direct discharge of the cells through resistive loads. The agreement between both types of data attest to the satisfactory functioning of the system.

It is seen that the effect of the film thickness upon the performance of oxygen and hydrogen electrodes is not very pronounced. With air as the oxidant, however, it is evident from the data in Fig. 8 that the thinner films result in better performances. This is reasonable in view of the lower permeability that would be anticipated for the heavier films, and hence the greater tendency towards blockage with nitrogen.

Since an important purpose served by the film is the prevention of electrode drowning, as well as gross leakage of the electrolyte through larger pores, a word is in order about these aspects of performance. Electrode drowning manifests itself by severe polarization over a narrow range of current density. It is therefore evident from the data for the hydrogen and oxygen electrodes in Figs. 7 and 8 that drowning is not a problem.

Some electrolyte leakage occurred with all of the electrodes used in this series of tests, but it was found to be concentrated in the boundary region between the active area and the peripheral Teflon rings. It was,

therefore, impossible to obtain meaningful quantitative data. Qualitatively, however, it was observed that the active electrode areas were freer from seepage droplets, the thicker the film.

It would, therefore, appear that practical electrodes, particularly air electrodes, will require an optimization between rate of seepage and gas accessibility. From the above, as well as repeated experiments with similar electrodes, it is our opinion that at the present state of development, film thicknesses between 0.79 and 2.4 mg Teflon/cm² are the most attractive with regard to overall performance.

Effect of Other Electrode Parameters and Processing Variables

With the platinum black catalyst several other electrode parameters and processing variables were examined briefly. These included: (1) effect of screen wire size, mesh, and material; (2) effect of pressure used in final sintering; (3) effect of ratio of catalyst to Teflon; (4) effect of amount of platinum and Teflon; and (5) effect of using a commercially available Teflon film for the surface layer.

Screen Characteristics - Changes in the supporting screens manifested themselves by affecting the cell resistance and the associated IR drop. Even in the small laboratory cells, electrodes constructed with 80-mesh, 3-mil platinum wire screens showed excessively high ohmic drops, particularly when electrodes with narrow tabs were used. At the other extreme were electrodes employing low-resistance silver screens with 7.5-mil wires and wide tabs. The 40- to 45-mesh platinum and nickel screens that were used in most of the work were intermediate in performance.

Sintering Pressure - Variation in the pressure used in preparing electrodes was not examined in detail nor over a wide range. Those prepared at the lowest pressure tested, 180 lb/in², were lacking in strength, although their electrical performance was excellent. With these electrodes, however, the gaskets from the cell, were capable of inducing appreciable flow of the catalyst-Teflon mix and failures occurred around the edges. In general, pressures of the order of 1800 to 3000 lb/in² were considered most satisfactory for the preparation of electrodes.

Ratio of Catalyst to Binder - The ratio of the amounts of platinum and Teflon could not be changed over a wide range with the procedures used. Electrodes of satisfactory strength and performance can be obtained within the range of platinum-to-Teflon weight ratios from 1:0.05 to 1:0.5. Most of the work was done with the ration 1:0.09 (i. e., 1 gram platinum black to 0.10 cc Teflon-30 solution).

Amount of Platinum and Teflon - Experiments were run with alkaline cells using electrodes containing from 17 to 45 mg platinum/cm² (a constant weight ratio of platinum-to-Teflon binder of 1:0.09 was used and the film thickness was maintained at 2.4 mg Teflon/cm²). Pronounced effects were not observed although the thinnest electrodes leaked excessively. Electrodes containing in the range 30 to 40 mg platinum/cm² appeared to be quite satisfactory and were adopted for most of the remaining work.

Commercial Films as Surface Coatings - While the major portion of the effort employed sprayed films of Teflon, a few electrodes were made with commercially available Teflon films that had a nominal thickness of 1/8 mil (obtained from Dielectrix, Inc.). These electrodes were prepared in the standard fashion except that the film was added in an extra pressing operation at the end of the regular procedures. These electrodes were operable at current densities of 500 to 600 ma/cm² on both hydrogen and oxygen.

In this connection it is of interest to note that the permeation rates shown in Table II were obtained for the film with the mass spectrometer*. Because all spectrometer peaks were established rapidly upon placing the gases on the high pressure side of the film, it was concluded that pores were present. Assuming linear relationships, the tabulated data correspond to permeation rates of 0.073 and 0.063 cc (STP) per minute per cm² of the 1/8-mil film for hydrogen and oxygen, respectively, at a pressure differential of 1 atm. The observed currents of about 500 ma/cm² call for gas consumption rates of about 3.4 and 1.75 cc/min for the hydrogen and oxygen. This would indicate that the film ruptured sufficiently during processing to permit the passage of the additional gas to the catalyst.

TABLE II
Permeation Rates for Dielectrix, Inc.
1/8-mil Teflon Film

Temp (°C)	permeation rate, P, in $\frac{\text{cm}^3 \text{ (STP)}}{\text{sec}}$. $\frac{\text{mm thickness}}{\text{cm}^2 \text{ area} \cdot \text{cm Hg pres.}}$					
	H ₂	He	O ₂	N ₂	Ar	SF ₆
28	5.1x10 ⁻⁸	2.7x10 ⁻⁸	4.4x10 ⁻⁸	6.8x10 ⁻⁸	2.45x10 ⁻⁸	—
53	2.4x10 ⁻⁷	1.6x10 ⁻⁷	1.45x10 ⁻⁷	1.3x10 ⁻⁷	1.2x10 ⁻⁷	2.55x10 ⁻⁸

* The authors are indebted to Dr. F. J. Norton for these measurements.

While the electrical properties of these electrodes were comparable with the others, seepage of electrolyte through the pores was also comparable.

Effect of Operating Conditions on Cell Performance

Several important operating parameters were varied during the course of the work. In particular, the effects of the liquid and gas pressure heads were considered, as was the effect of the electrolyte concentration. In addition, tests were made to determine the need for an external circulation loop and reservoir.

Effect of Electrolyte Head - Polarization data were obtained for several alkaline cells as the electrolyte heads were varied over the range 3 to 24 inches above the tops of the electrodes. During these tests the circulating loop to the reservoir was not closed. Instead, a "stand-pipe" arrangement was used with a thin tube filled with electrolyte serving to provide the hydrostatic pressure. Hydrogen and oxygen gas pressures of about 2 to 3 inches of water were used. The range of pressures covered should easily include the highest excess electrolyte pressures which will be encountered in practical size cells having electrodes up to 20 inches on a side.

As evidenced by the data in Fig. 9, increasing the liquid head results in little change in the electrical performance of the cell or in that of the individual electrodes. The slightly poorer overall polarization curve obtained with the largest liquid head does, however, appear to be real and undoubtedly reflects some penetration of the electrolyte into the pores of the electrodes. Reduction of the pressures reversed this effect.

In the small laboratory cells the pressure gradient varies by only 1 1/2 inches from the top of the electrode to the bottom. In a practical device, with its larger electrodes, the gradient will vary considerably more. These experiments indicate, however, that the electrical performance at the different levels will not differ significantly.

Qualitative observations on seepage of electrolyte through the electrodes were normal; i. e., the rates increased with the excess hydraulic pressure.

Effect of Gas Pressure - In looking at the effect of gas pressure on cell performance, a range from 1 inch to 22 inches of water was covered. The cells were arranged with the electrolyte in a closed loop with a head of

2 or 6 inches above the tops of the electrodes. In these tests a 3/8 inch thick spacer was used between the electrodes to minimize the danger of bridging the gap should gases bubble into the electrolyte. The cells, therefore, had a somewhat higher internal resistance than normal. As a result the overall polarization curves obtained with these cells were slightly inferior to others in this paper. It was found that the cells could be operated with gas pressures exceeding the hydraulic head of the electrolyte by as much as 20 inches of water without bubbling into the electrolyte occurring.

Representative polarization data obtained with different gas pressures are shown in Fig. 10 for an alkaline electrolyte. Similar results were obtained with an acid electrolyte. These curves show no pronounced effects that can be attributed directly to changes in the gas pressures. Indeed, the data were exceptionally reproducible even at the higher current densities.

At the higher current densities the temperatures in the cells were also high. For example, with cell LFC-307 containing 6 M KOH as electrolyte at a current density of 580 ma/cm², an electrolyte temperature of 83°C was measured. Under these conditions the anode and cathode temperatures were 82° and 88°C, respectively, and the reservoir measured 38°C. Similar temperatures were obtained with acidic electrolytes. At such temperatures the partial pressure of water is fairly high, particularly at the water-producing electrode where the electrolyte is diluted. For this reason, as well as the fact that cell performance at high current densities is sensitive to gas flow rate, it appears highly likely that steam blanketing of the electrodes may occur.

Effect of the Electrolyte Concentration - As noted in the previous section, some cells operating on hydrogen and oxygen and employing 6 M KOH or 5 N H₂SO₄ as the electrolytes have shown evidence of some steam blanketing at the electrodes. In an effort to reduce this effect, a number of cells were run with more concentrated electrolytes over which the vapor pressure of water was considerably less.

When 12 M KOH was used there was, indeed, a slight improvement in performance at high current densities. Unfortunately, however, because of its higher resistivity, this electrolyte tended to heat more than 6 M KOH at corresponding current densities. In addition, its higher viscosity resulted in less circulation through the external loop and this also contributed to a higher temperature in the cell, e. g., 96° vs 83°C at a current density of

580 ma/cm². This attempt to reduce the vapor pressure of the water was therefore largely self defeating. In general, however, 12 M KOH appeared to be an attractive electrolyte. In particular, its higher viscosity resulted in lower seepage rates through the electrodes than are seen with 6 M KOH.

Attempts to examine the effect of increasing the electrolyte concentration with the acid were unsatisfactory. Sulfuric acid is less effective than potassium hydroxide in reducing the vapor pressure of water, and a 23 N solution is required to accomplish the reduction equivalent to 12 M KOH. This concentration of acid proved unsatisfactory. When it heated to a temperature of 60° to 70°C, direct reaction with the hydrogen occurred, and hydrogen sulfide formed and poisoned the fuel electrode. A similar behavior was observed with 17 N H₂SO₄, but in this case when the temperature reached 80° to 90°C.

Effect of Electrolyte Circulation - Because an external circulation loop such as that used in much of the present work may prove cumbersome in the designing of practical cells, it was of interest to determine whether this is required for satisfactory operation. For this purpose an air-breathing, acid cell was placed in operation without any external circulation. In stead, a small funnel was attached to the top inlet tube on the electrolyte chamber, and water - to compensate for evaporation losses - was added directly to the cell chamber.

That adequate mixing of the electrolyte can be achieved in this way was clearly attested to by flat operation at 0.68 volt and 88 ma/cm² over 25-hour periods both during operation of the cell in this fashion and during operation with a thermal loop when the makeup water was added to the reservoir. Even with larger cells, thermal mixing within the electrolyte chamber should be more than adequate to prevent stratification of the electrolyte when the water is introduced at the top. If stratification were to occur and a water layer formed at the top, the resistance across that layer would be much greater than in the lower acidic region. The current would, therefore, be concentrated at the bottom of the cell and more power would be dissipated there than at the top. The heat so generated would therefore be distributed in a way to promote convective mixing and thereby destroy concentration gradients within the electrolyte.

If desired, however, makeup water could be introduced at the bottom of the cell chamber. In this case density differences between the makeup water and the electrolyte already in the cell would contribute to the mixing.

Alternative Electrocatalysts

A few exploratory experiments were performed with alternative electrocatalysts. These included silver and activated carbons. Electrodes of both types performed reasonably well with oxygen. This is shown by the data in Fig. 11. The silver electrode used in cell LFC-264 contained approximately 70 mg Silflake-131 (Handy and Harmon) and 7 mg Teflon binder/cm². It was coated with a surface film containing 2.4 mg Teflon/cm². The platinized carbon electrode of cell LFC-282 contained 17 mg amorphous carbon containing 10% platinum and 3 mg Teflon binder/cm². It too was coated with a surface film containing 2.4 mg Teflon per cm². The anodes in both of these cells were made with platinum black.

These data are included merely to indicate the promise of some of these less expensive materials as practical electrocatalysts. Actually, the carbon-base material has shown even better performance with both oxygen and hydrogen in the earlier matrix type cells (8). This implies strongly that the carbon electrode of the present example does not represent the optimum in wetting control.

Performance During Continuous Operation

Seven cells have been placed on continuous operation at current densities of 88, 176, or 263 ma/cm² for periods of from 5 days to over 5 months. The first cell was operated with forced circulation of the electrolyte. All of the remaining units were operated with thermal loops.

The hydrogen supply was sufficiently pure to permit operation on static heads of gas with an occasional short purge (a few seconds) to sweep out impurities that slowly accumulated in the fuel electrode's gas chamber. Because the impurity level of the oxygen was higher, it was necessary to continuously vent a slow stream of oxygen from the cells; a rate of less than 1 cc/min was maintained.

Graduated traps in the vent lines permitted the collection of liquid that accumulated in the gas chambers. This included seepage as well as water which distilled from the electrodes to the faceplates of the cells. All was recycled back to the reservoirs. To minimize seepage, electrolyte heads were held to about 1 inch above the tops of the electrodes.

During air operation with a fully exposed electrode, more water was evaporated than was produced in the cell reaction. In such cases makeup water was added periodically to the reservoir.

During operation on oxygen the water formed in the cell reaction gradually diluted the electrolyte so that periodic replacement was required. The need for replacement was generally indicated by a decline in cell performance; the response of the cell to fresh electrolyte was immediate. During early tests about 80 cc of electrolyte were used in charging a system. Later this was increased to about 250 cc in order to extend the periods between replacements.

Some representative performance data are summarized in Fig. 12 through 15. Shown are cell voltages on load as well as polarization curves obtained after various periods of operation. No cell failures occurred during these tests apart from leaks which developed in cell housings.

Cell LFC-260 was one of the first cells to be assembled. Its electrodes are reinforced with 80-mesh, 3-mil wire, platinum screens having narrow tabs. As a result its internal resistance was high, 0.12 ohm, and a drop of about 0.15 volt occurred in the tabs themselves at the operating current of 2 amperes (176 ma/cm^2). Nevertheless, this acid cell gave excellent performance on hydrogen and air for over 160 days as attested to by the data in Figs. 12 and 13.

A word is in order about the performance of this cell during the first 52 days. During this period silicone rubber gaskets were used on the cell. Gradual attack from the acid produced silica which accumulated in the pores of the electrodes. On the 52nd day the cell was disassembled and the electrodes were leached with warm sodium hydroxide. After reassembly with poly(ethylene-butene) copolymer gaskets, the cell performed excellently for over 110 additional days.

Cell LFC-269 contained the same electrodes as provided the data in Fig. 5. They were reinforced with 40-mesh, 4.5-mil wire, rolled nickel screens having wide tabs. This alkaline cell had a considerably lower resistance than LFC-260, i. e., 0.06 ohm. It was operated on hydrogen and oxygen for over 140 days at the current densities indicated in Fig. 14. During the first 19 days a small reservoir charged with 80 milliliters of electrolyte was used. This was subsequently changed to a larger reservoir with charges of about 250 milliliters of fresh electrolyte, although the amount was reduced again upon switching to 12 M KOH. In general, the performance of this cell was excellent, and as shown by the polarization data in Fig. 15 there was no decline in its ability to handle overloads.

SUMMARY AND CONCLUSIONS

The structure of Conducting-Porous-Teflon electrodes has been improved with regard to strength, conductivity, and wetting characteristics. In their new form these very thin electrodes (5 to 10 mils thick) may be employed with aqueous electrolytes without the need for the matrix-type support previously used. The result is a fuel cell having excellent performance characteristics. These include an ability to operate on air at practical current densities of 100-200 ma/cm². In other work the new electrodes have also been shown to have excellent performance characteristics with hydrocarbon fuels and with methanol.

The new cells may be operated with the electrolyte circulated through an external loop by thermal pumping, or the electrolyte may be used without such circulation.

A number of cells have been operated continuously for periods of months with encouraging results. One of our first hydrogen-oxygen cells was operated with an acid electrolyte and air as oxidant at a current density of 176 ma/cm² for over 5 months. A similar alkaline cell, was operated on hydrogen and oxygen at current densities of 263 and 88 ma/cm² for a similar period.

ACKNOWLEDGEMENTS

The authors are indebted to H. A. Liebhafsky, E. J. Cairns, and W. T. Grubb for helpful discussions during the course of this investigation. They also appreciate the assistance of F. J. Norton who measured the permeability of one of the Teflon films, and that of E. F. Koch and R. R. Russell who obtained the photomicrographs of electrodes.

REFERENCES

1. J.S. Bone, S. Gilman, L.W. Niedrach and M.D. Read, Proceedings 15th Annual Power Sources Conference, Atlantic City, N.J., P. 47 (1961).
2. L.W. Niedrach, Belgian Patent No. 617, 375 (1962).
3. W.T. Grubb and L.W. Niedrach, Proceedings 17th Annual Power Sources Conference, Atlantic City, N.J., P. 69 (1963).
4. W.T. Grubb and L.W. Niedrach, This Journal, 110, 1086 (1963).
5. W.T. Grubb and C.J. Michalske, Electrochemical Society New York Meeting, October 1963, Extended Abstract of the Battery Div. P. 98.
6. E.J. Cairns and D.C. Bartosik, Electrochemical Society, Toronto Meeting, May 1964, Extended Abstracts of the Theoretical Division.
- 6a. Information Bulletin No. X-50d, E.I. duPont deNemours & Co.
7. K. Kordesch and A. Marko, Journal of Electrochemical Society, 107, 480 (1960).
8. L.W. Niedrach, unpublished results.

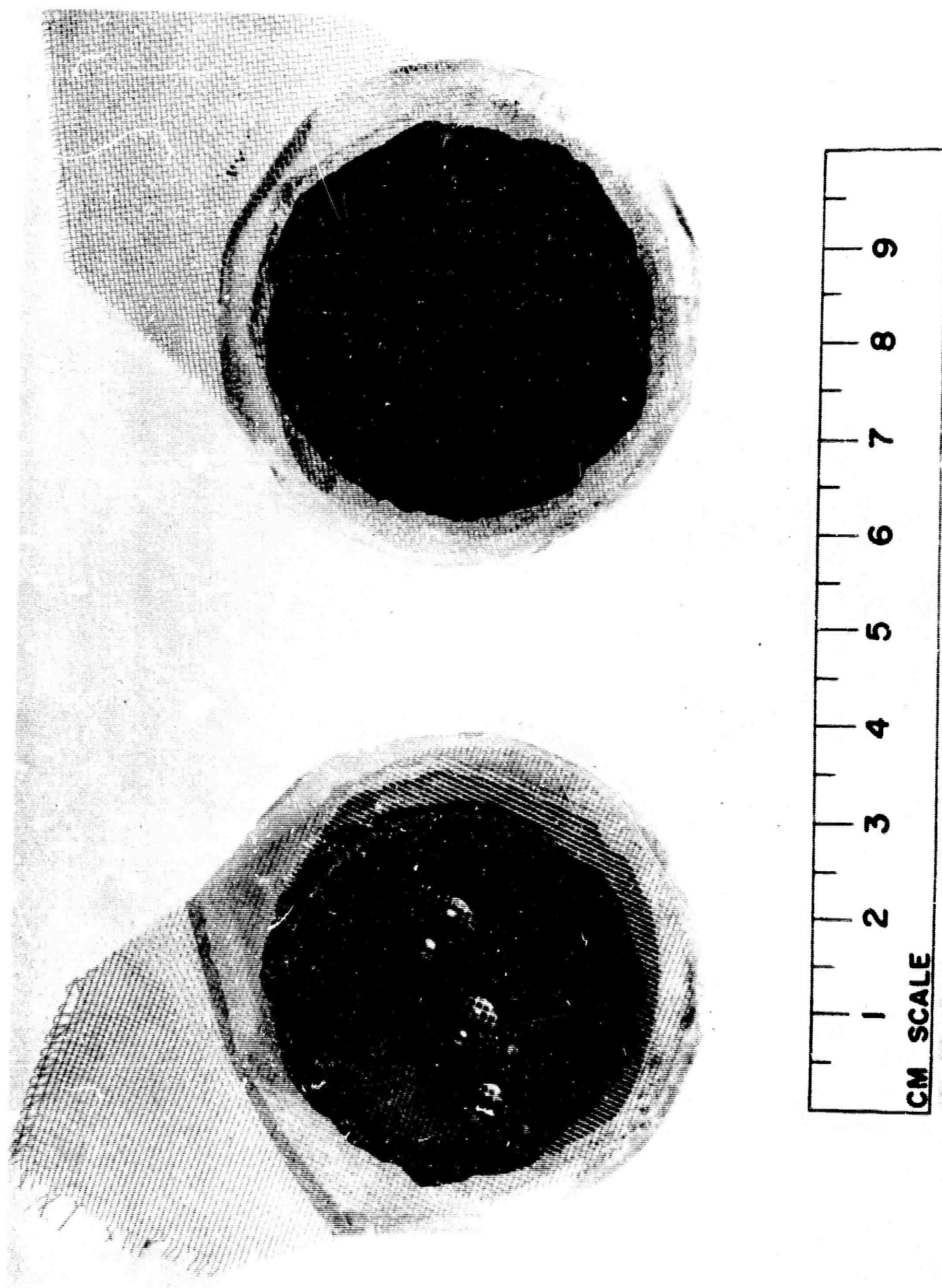


Fig. 1. Typical Electrodes Showing Wetting Characteristics

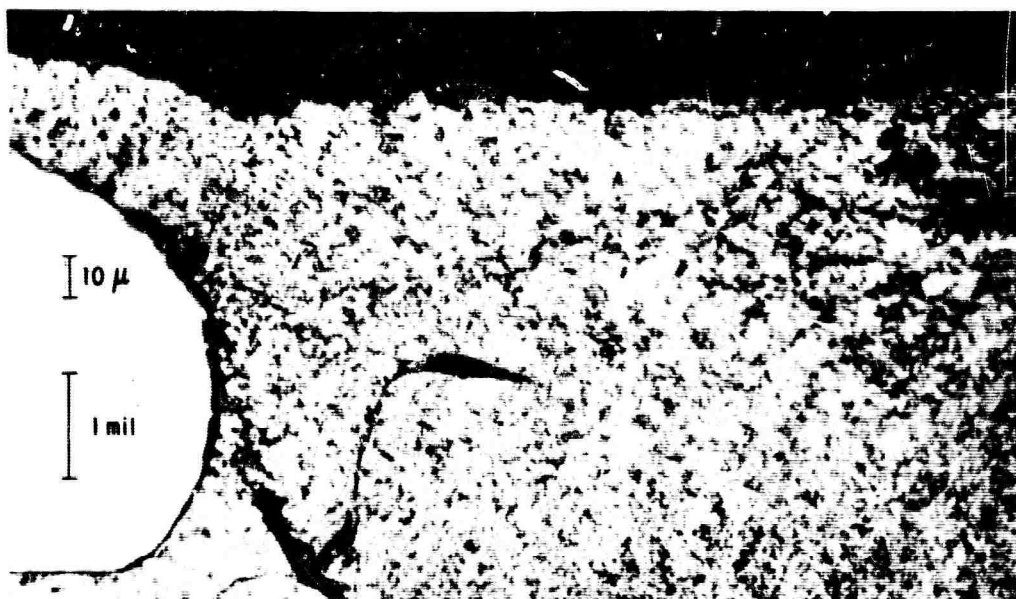


Fig. 2. Photomicrograph of a Sectioned Electrode Showing the Surface Film on One Side. (Electrode No. 375. Body: 34 mg Pt black, 3.1 mg Teflon/cm²; Film: 2.4 mg Teflon/cm²; Nickel screen 40-mesh; 4.5 mil wire.) 500x



Fig. 3. Electron Micrograph of Microtomed Section of an Electrode Showing Surface Film. (Electrode No. 375.) 10,000x

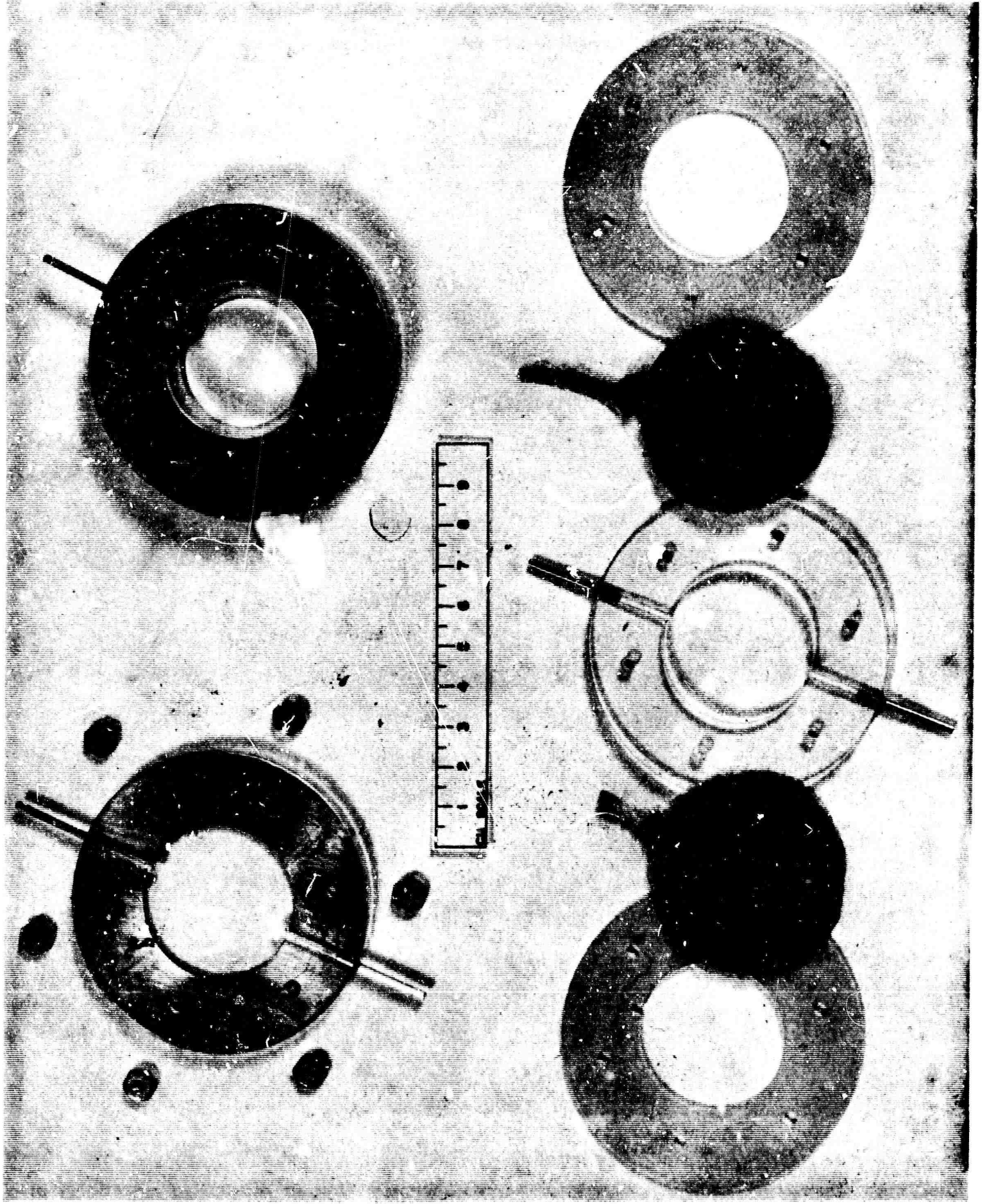


Fig. 4. Exploded View of Test Cell

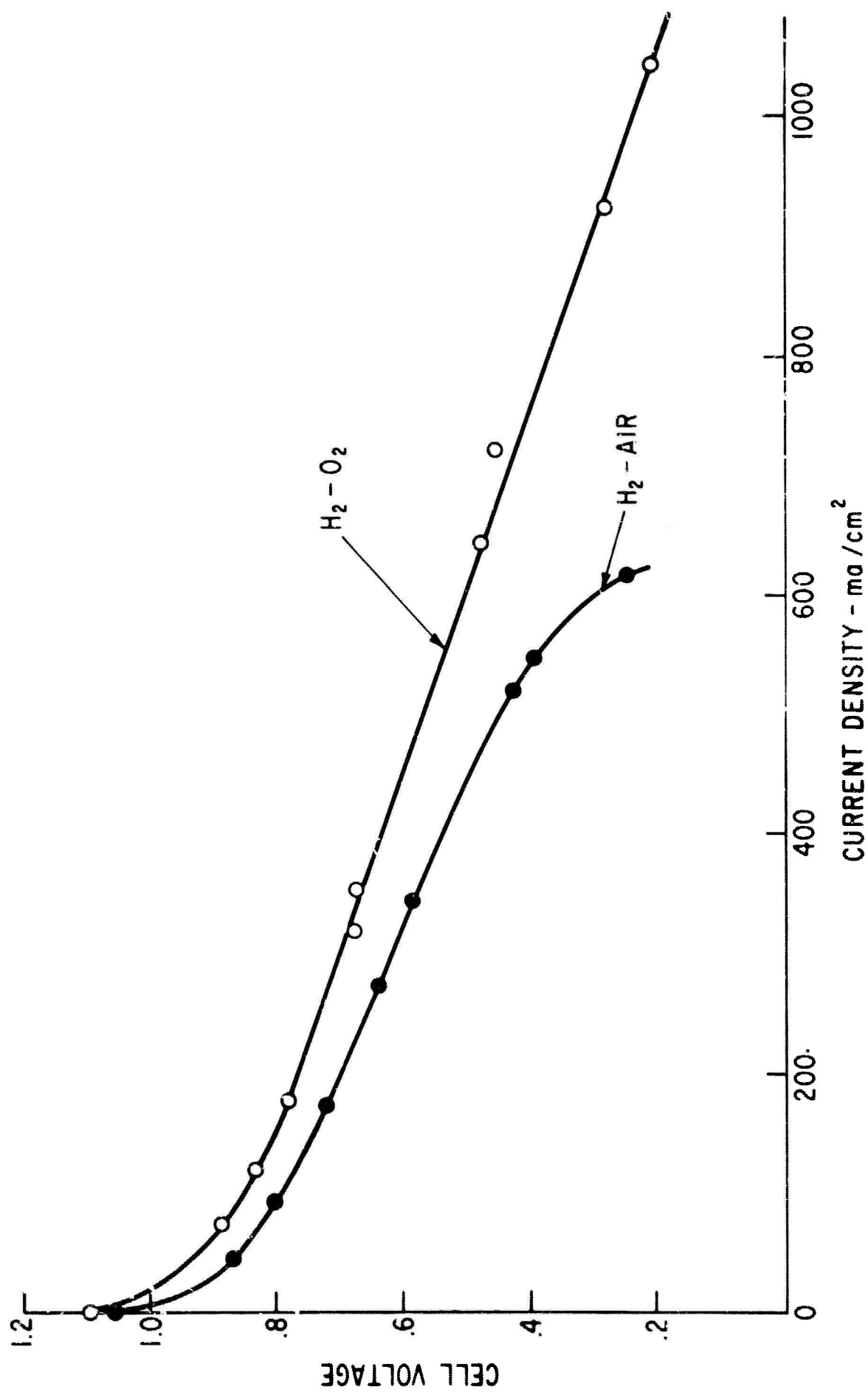


FIGURE 5. PERFORMANCE WITH ALKALINE ELECTROLYTE.

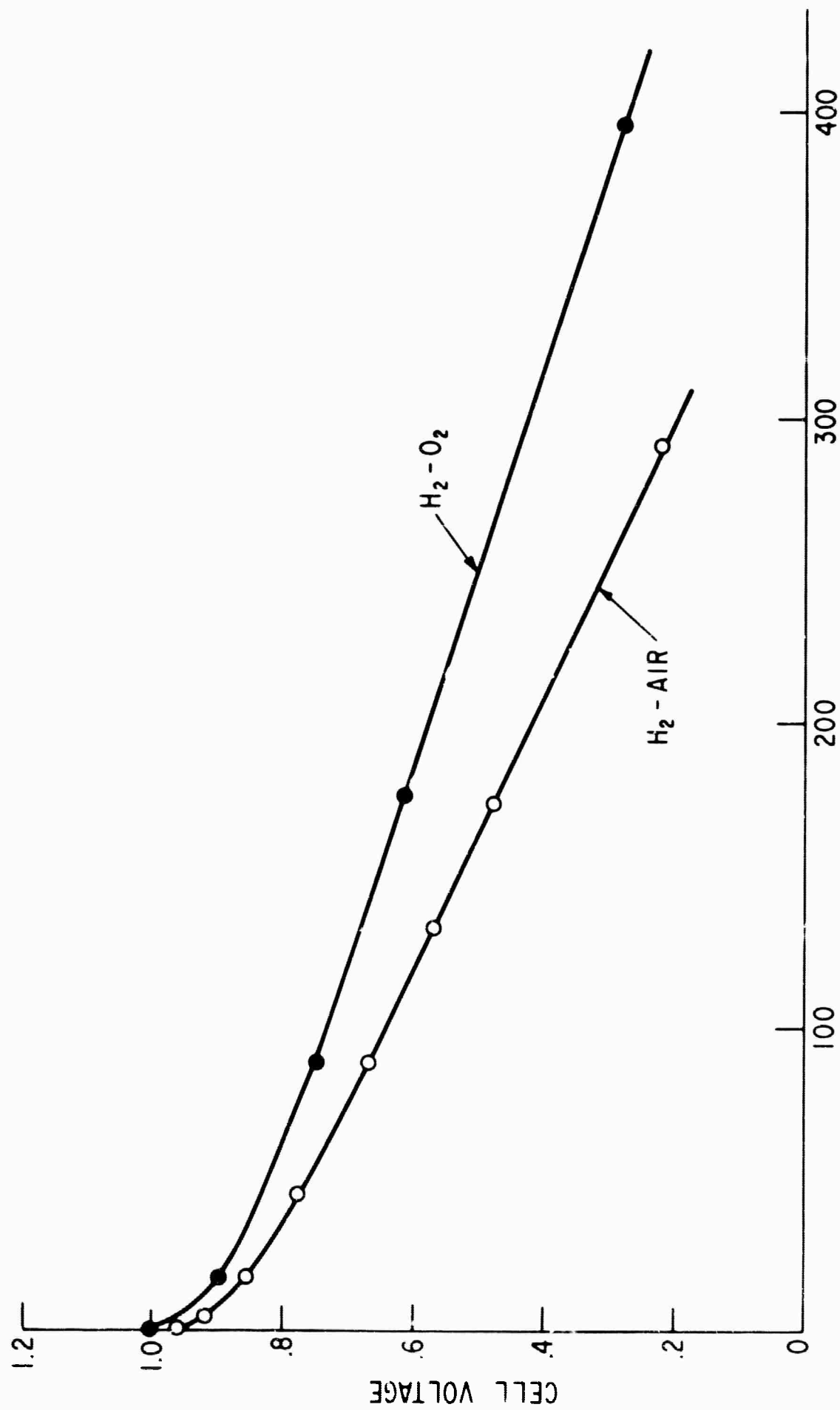


FIGURE 6. PERFORMANCE WITH ACIDIC ELECTROLYTE.

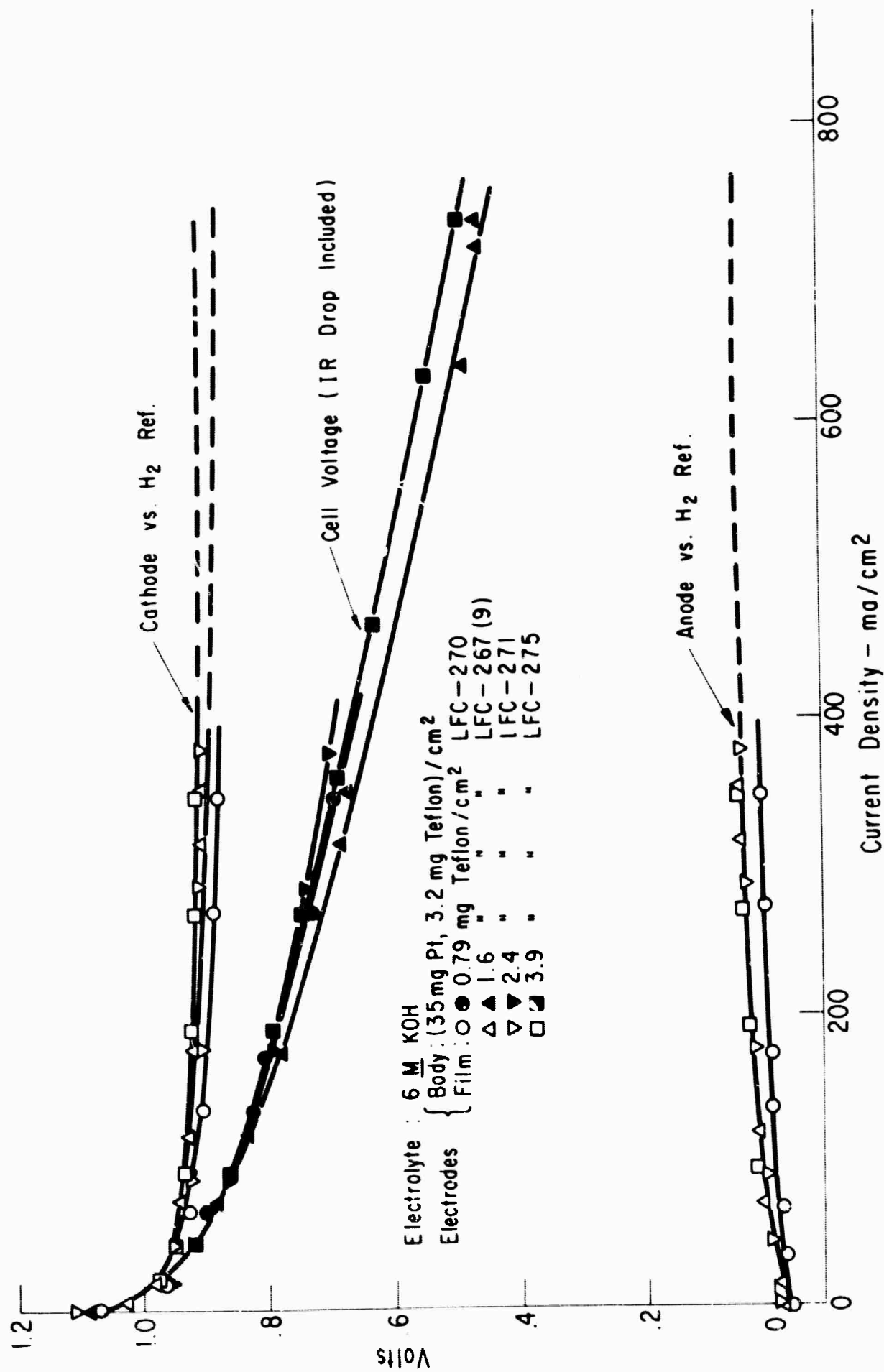


FIGURE 7. EFFECT OF FILM THICKNESS ON PERFORMANCE WITH H₂ AND O₂

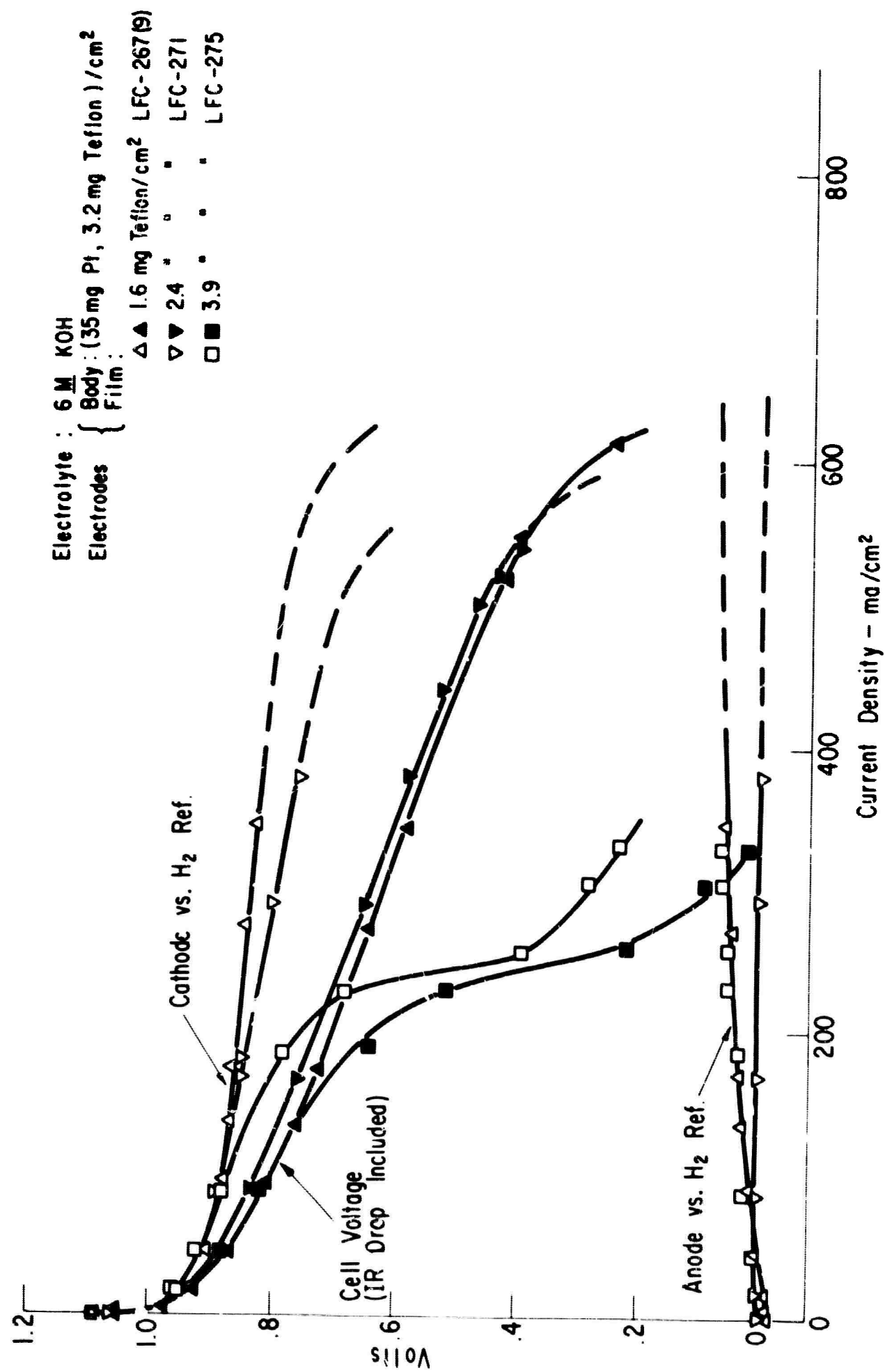


FIGURE 8. EFFECT OF FILM THICKNESS ON PERFORMANCE WITH H₂ AND AIR.

Cell LFC-269

Electrolyte : 6 M KOH

Electrodes { Body : (35 mg Pt, 3.2 mg Teflon) / cm²
 Film : 1.6 mg Teflon/cm²

Gas Pressures : ~2" H₂O

Electrolyte Head : ▽ ▴ ▴ ▴ 3" Above Top of Electrode

○ ●

□ ■

◇ ◆

6" 12" 24"

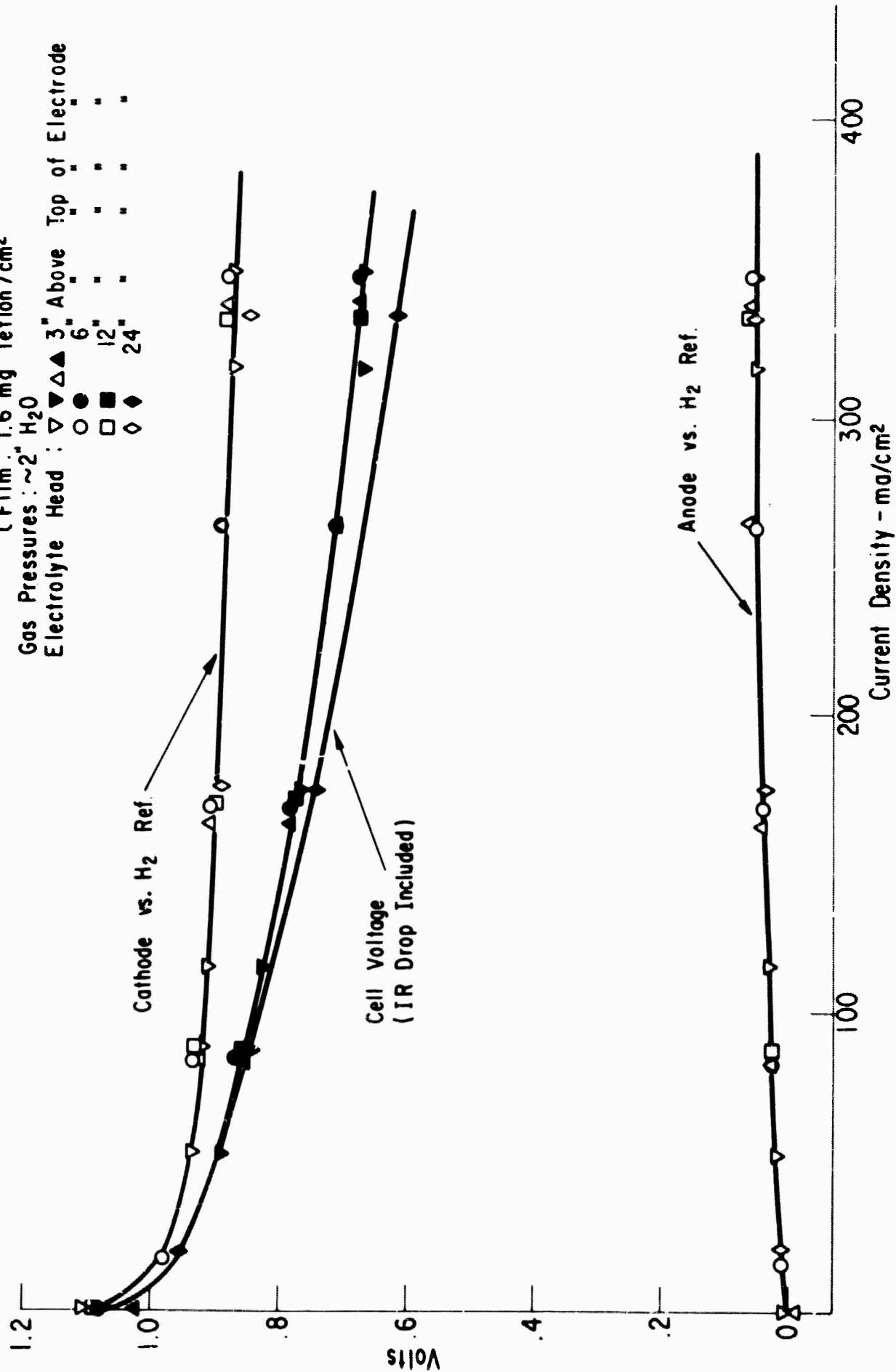


FIGURE 9. EFFECT OF ELECTROLYTE HEAD ON THE PERFORMANCE OF AN ALKALINE H₂ - O₂ CELL

CELL LFC-307

ELECTROLYTE : 6 M KOH
 ELECTRODES { BODY : 40 mg Pt, 3.6 mg TEFLON/cm²
 FILM : 2.4 mg TEFLON/cm²
 ELECTROLYTE HEAD : 6" ABOVE TOP OF ELECTRODE
 GAS PRESSURE : Δ 1" H₂O
 O 6" "
 □ 15" "

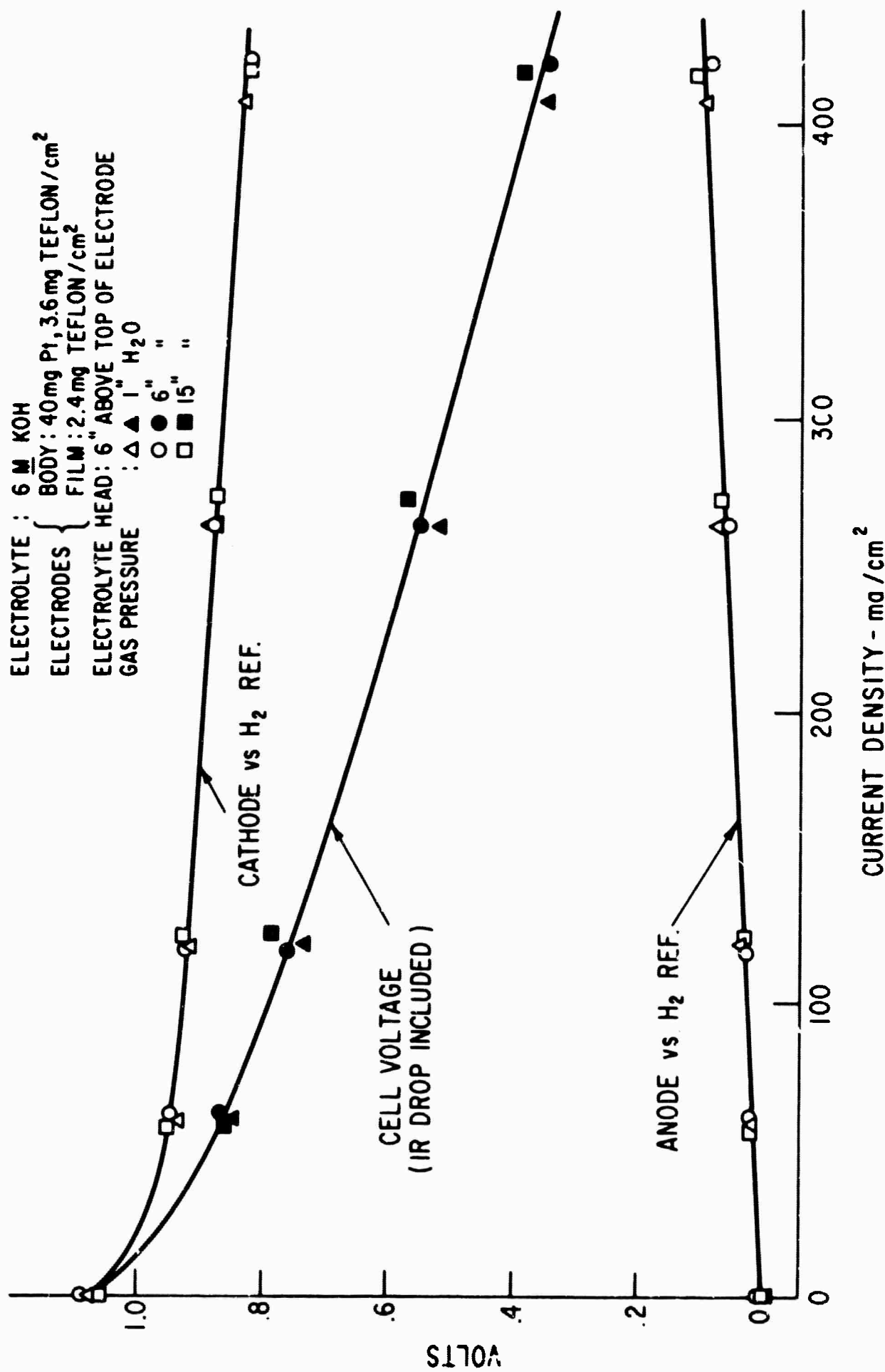


FIGURE 10. EFFECT OF GAS PRESSURE ON THE PERFORMANCE OF AN ALKALINE H₂-O₂ CELL.

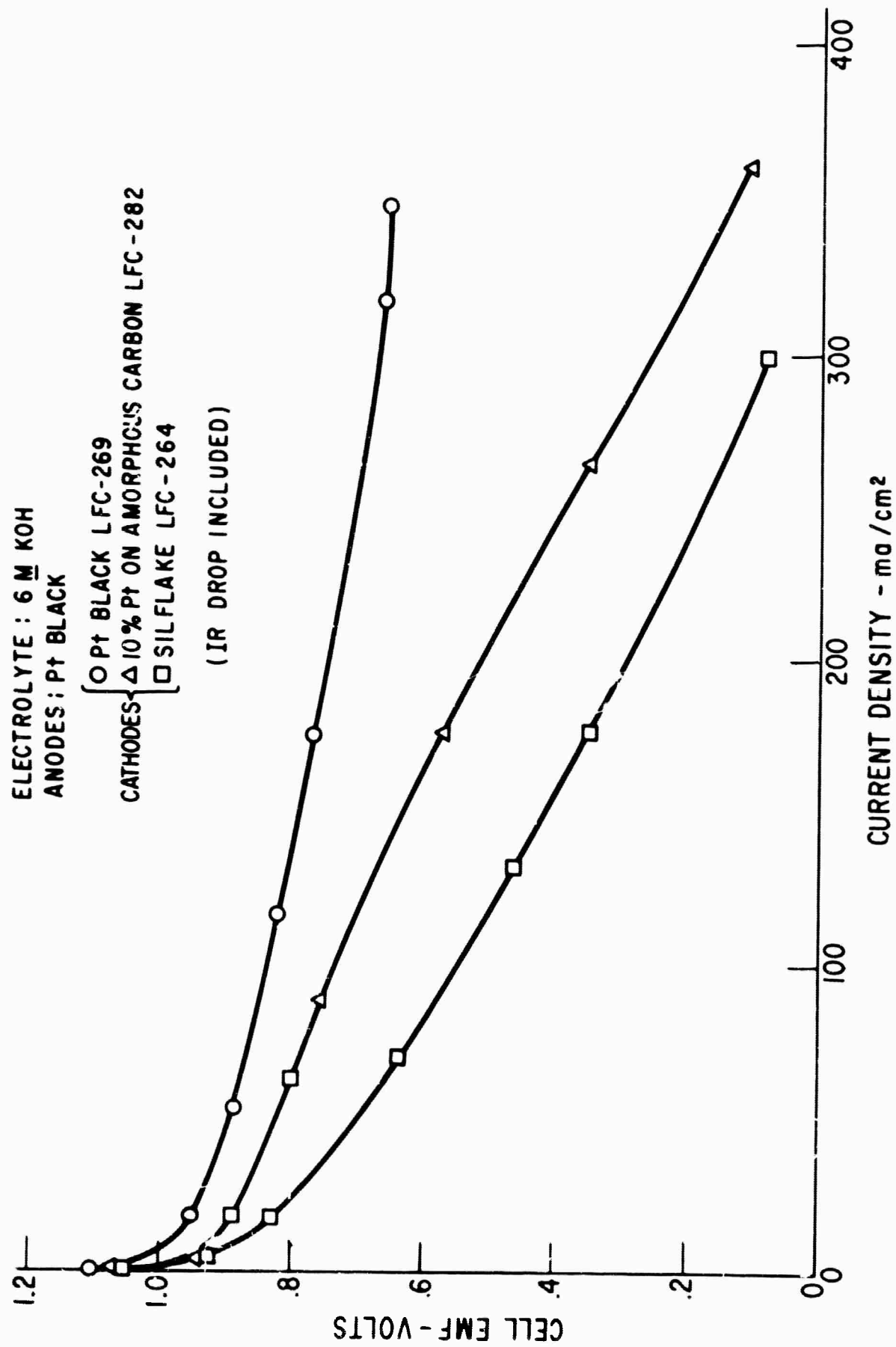
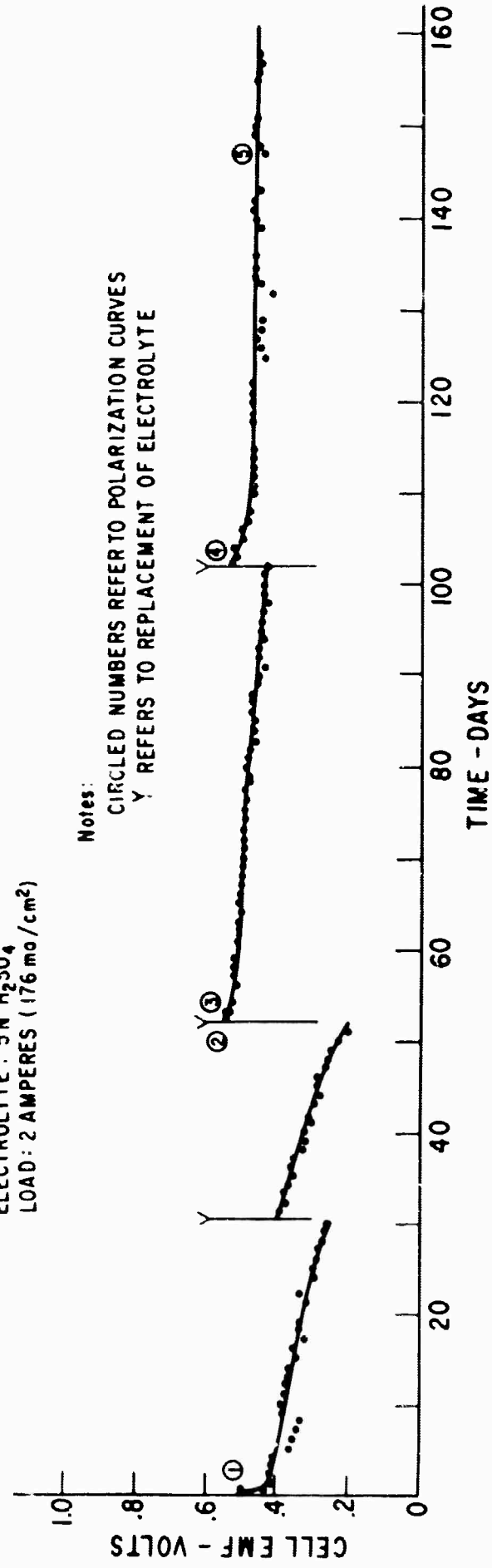


FIGURE 11. PERFORMANCE OF CELLS WITH VARIOUS OXYGEN ELECTRODE CATALYSTS

CELL LFC 260

ELECTRODES: PLATINUM BLACK
ELECTROLYTE: 5N H₂SO₄
LOAD: 2 AMPERES (176 ma/cm²)



Notes:

CIRCLED NUMBERS REFER TO POLARIZATION CURVES
Y REFERS TO REPLACEMENT OF ELECTROLYTE

FIGURE 12. PERFORMANCE OF ACIDIC H₂-AIR CELL WITH PLATINUM BLACK ELECTRODES ON CONTINUOUS LOAD.

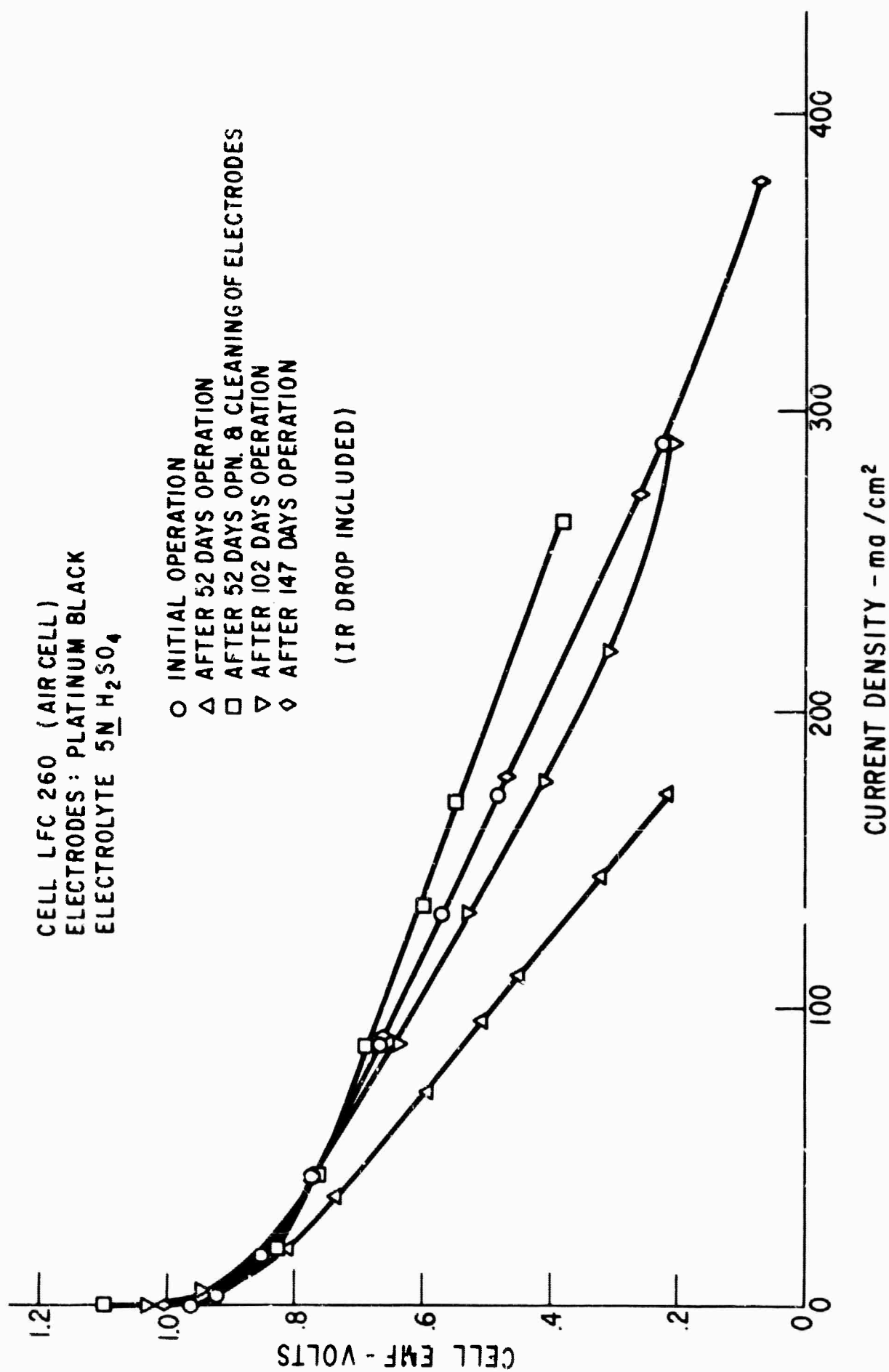


FIGURE 13. POLARIZATION CURVES OBTAINED DURING TESTS ON CONTINUOUS LOAD

CELL LFC 269

ELECTRODES: PLATINUM BLACK

ELECTROLYTE: 6.8 12 M KOH

LOAD: 1 AMPERE (88 ma/cm²)

8.3 AMPERES (263 ma/cm²)

Note:

CIRCLED NUMBERS REFER TO POLARIZATION CURVES

Y REFERS TO REPLACEMENT OF ELECTROLYTE

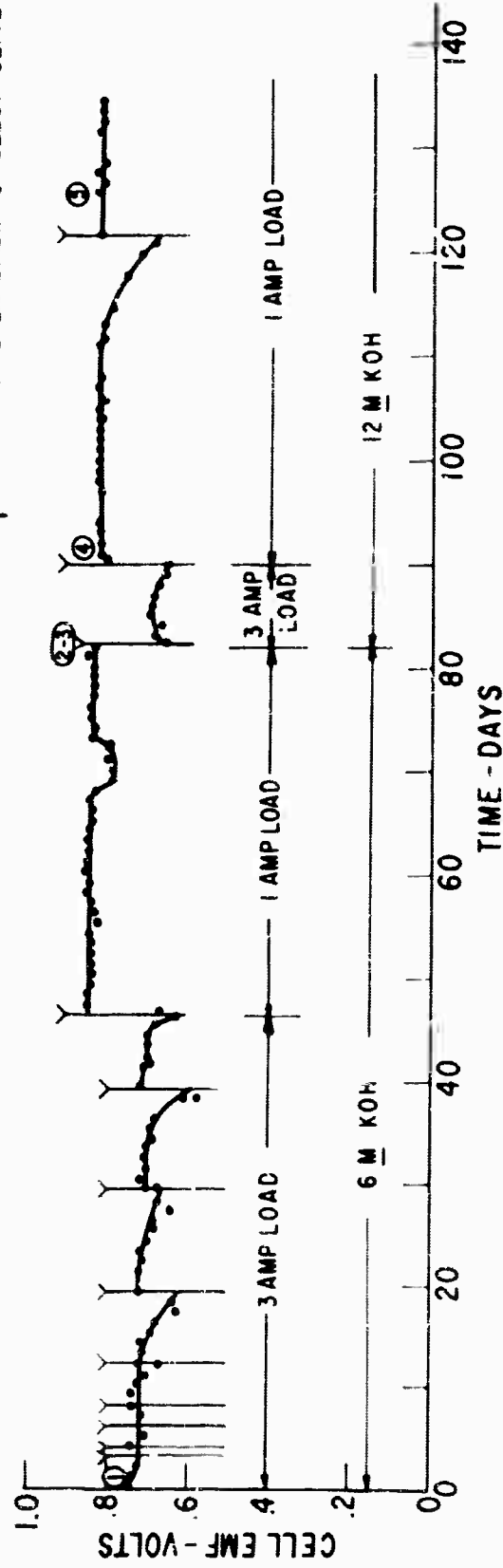


FIGURE 14. PERFORMANCE OF ALKALINE H₂-O₂ CELL WITH PLATINUM BLACK ELECTRODES ON CONTINUOUS LOAD.

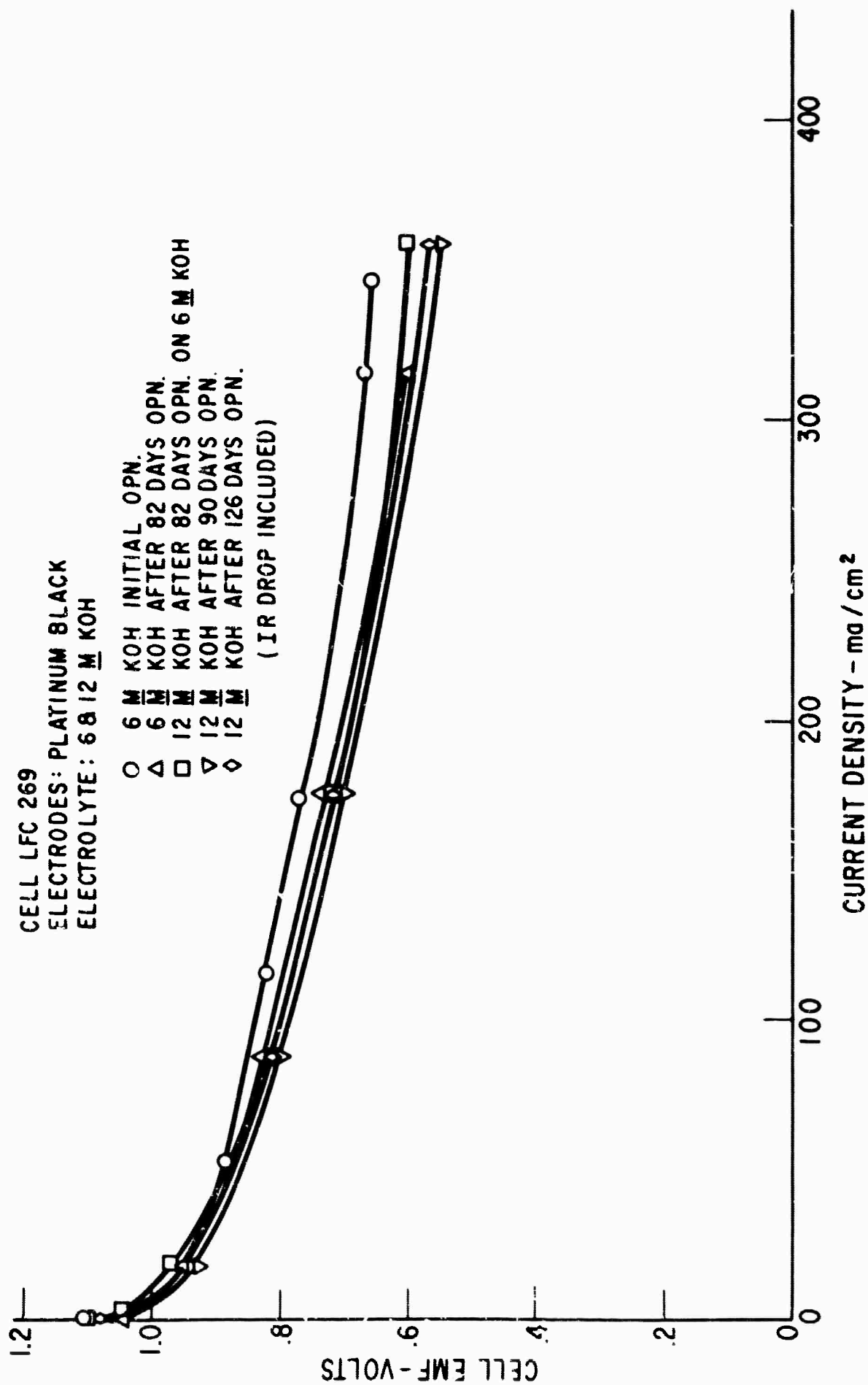


FIGURE 15. POLARIZATION CURVES OBTAINED DURING TESTS ON CONTINUOUS LOAD